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# The Interaction of Chromium(III) Ion with Hydroxide Ion

*An experiment for the undergraduate  
inorganic laboratory*

The transition-metal ions in aqueous solution can serve as interesting and instructive experimental examples of a variety of types of chemical behavior. The transformation from one species to another can often be correlated by the student with changes in color or with the appearance or disappearance of a precipitate. In the interactions with hydroxide ion, at least three different types of reaction may be considered. The first is protolysis, involving the transformation of coordinated  $\text{H}_2\text{O}$  to coordinated  $\text{OH}^-$ , which may be treated like the equilibria of a polyprotic acid or in terms of the formation of hydroxo-complexes. The second is the formation of a sparingly soluble hydroxide, treated in terms of solubility-product equilibria. Students must, of course, be made aware of the varying and variable nature of the oxides, hydrous oxides, hydroxides, etc., which actually form. It is, however, a convenient shorthand to refer to these substances generically as hydroxides and to write the formulas as such. (The possible formation of basic salts will not be considered in this paper.) Also, for purposes of abbreviation, formulas of aquo- and hydroxo-complexes will be written without inclusion of coordinated water, as  $\text{CrOH}^{2+}$  for  $\text{Cr}(\text{H}_2\text{O})_5\text{OH}^{2+}$ . The third reaction to be considered is the formation of polymeric species (1). The experiment summarized here is included in the second-year inorganic chemistry course (given in place of qualitative analysis) for chemistry majors.

Qualitative experiments with chromium(III) will demonstrate the existence of several solute species besides  $\text{Cr}^{3+}$ : A solution of chromium(III) nitrate is markedly acidic; as sodium hydroxide is added, the color changes from violet to green, and not until nearly equimolar base has been added does a precipitate form;

the green solution formed by treating  $\text{Cr}(\text{OH})_3$  with excess base suggests the existence of anionic species. Chromium(III) is indeed notorious with regard to the formation of polymers, and authors frequently comment on the irreducibility of results (2). Nonetheless, it possesses an advantage over many other cations that form polymers at higher  $\text{pH}$ , in that reactions involving the rupture of a chromium-ligand bond are slow (3) (i.e., the complexes are substitution-inert) and thus the formation of bridged polymers cannot occur as rapidly as the proton-transfer reactions which involve only the coordinated ligands. Consequently, at lower  $\text{pH}$ , an approach to a metastable equilibrium involving the monomeric species can be achieved. In basic solution, however, where the rate of polymerization is greatly increased, this simplifying assumption is likely to be invalid.

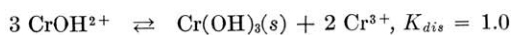
## Acidic Solutions

The  $\text{pH}$  of a solution of a chromium(III) salt is not expected to yield a reliable value of the acidity constant<sup>1</sup> of  $\text{Cr}^{3+}$  ( $K_{a1} = 1.3 \times 10^{-4}$ ) due to the low buffer index of the solution and to the fact that the measured hydrogen-ion concentration must be squared in the computation. The addition of *aq*  $\text{NaOH}$ , however, yields a  $\text{Cr}^{3+} - \text{CrOH}^{2+}$  buffer, from the  $\text{pH}$  of which  $K_{a1}$  can be determined. Although not of quantitative significance in the described experiment, the distinction between the thermodynamic equilibrium constant and

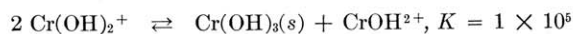
<sup>1</sup> Equilibrium constants quoted are taken or computed from the source listed in (4). An extensive and useful tabulation of such data may be found in (5).

the experimental equilibrium quotient (based on concentrations) should be made.

Note that an appreciable concentration of  $\text{CrOH}^{2+}$  can be formed before  $\text{Cr}(\text{OH})_3$  precipitates:



On the other hand,  $\text{Cr}(\text{OH})_2^+$  is unstable with respect to disproportionation:



and never reaches significant concentrations. Thus, in a solution containing  $c$   $M$   $\text{Cr}(\text{III})$  and  $b$   $M$  strong base, the effective proton condition, before formation of precipitate, is:

$$[\text{CrOH}^{2+}] = b + [\text{H}^+]$$

and, from the material balance,

$$[\text{Cr}^{3+}] = c - [\text{CrOH}^{2+}]$$

The disproportionation constant for  $\text{CrOH}^{2+}$ ,  $K_{dis}$ , can be estimated from the quantity of base required to form a permanent precipitate. Then the solubility product of  $\text{Cr}(\text{OH})_3$  ( $5 \times 10^{-31}$ ) can be computed from the  $pH$  at this point (using for both calculations the concentrations of predominant solute species given from the stoichiometric relations above), or from  $K_{sp} = K_w^3 / (K_{a1}^3 K_{dis})$ , where  $K_w$  is the autoprotolysis constant of water.

That this final system, containing  $\text{Cr}^{3+}$ ,  $\text{CrOH}^{2+}$  and a trace of  $\text{Cr}(\text{OH})_3(s)$ , is subject to slow polymerization is shown by the fact that the precipitate will disappear after a time. This is a result of the gradual conversion of  $\text{CrOH}^{2+}$  into the dimer ( $\delta$ )  $\text{Cr}_2(\text{OH})_2^{4+}$ , and then into higher polymers, which allows the equilibrium represented by  $K_{dis}$  to be shifted to the left. The polymerization phenomenon is greatly accentuated at elevated temperatures, where it will be noted that the  $pH$  drops markedly. Similarly, it can be seen that a solution of  $\text{Cr}(\text{NO}_3)_3$ , on being heated, turns from the violet of  $\text{Cr}^{3+}$  to the green of polymer and becomes more acidic.

### Alkaline Solutions

Although solutions of  $\text{Cr}(\text{OH})_3$  in base (to be referred to hereafter as "chromite") presumably contain anionic species, there seems to be no clear evidence as to whether a monomer such as the expected  $\text{Cr}(\text{OH})_4^-$  actually exists in them. The solubility data of Fricke and Windhausen (?) show, for consistently treated samples, a constant ratio of chromite to hydroxide, but this relation would be satisfied for any  $\text{Cr}(\text{III})$  species with charge of 1-, regardless of degree of polymerization. The fact that the solubility of  $\text{Cr}(\text{OH})_3$  in base depends on the time of contact with solution (first rising, then falling) and on the past history and quantity of solid indicates changes both in the nature of the solid and in the kinds of solute species present.

When 0.5  $M$   $\text{NaOH}$  is added to 0.5  $M$   $\text{Cr}^{3+}$ , the quantity of base required just to dissolve the precipitate first formed is fairly reproducible and corresponds to a ratio, (chromite)/( $\text{OH}^-$ ) of about 0.5. If, however, the  $\text{Cr}^{3+}$  is added to the  $\text{OH}^-$ , precipitation does not begin until this ratio is considerably larger than 0.5. Moreover, the incipient precipitate often will redissolve on vigorous shaking, and, with care, a considerable additional quantity of  $\text{Cr}^{3+}$  may be added before an obviously perma-

nent precipitate forms. The phenomenon may be explained as peptization of the precipitate, or, what amounts to the same thing, the extensive formation of polymeric anions. As a further indication that polymerization has taken place, it can be observed that when chromite solutions are treated with excess acid, the green color of polymer, rather than the violet of  $\text{Cr}^{3+}$ , is obtained.

### The Experiment

0.5  $M$   $\text{NaOH}$  is added gradually to 0.5  $M$   $\text{Cr}(\text{NO}_3)_3$  until it is present in considerable excess and the various qualitative changes which take place are noted.

The  $pH$  of  $\text{Cr}(\text{NO}_3)_3$  solution is measured. Then the  $pH$  of a  $\text{Cr}(\text{NO}_3)_3$  solution containing  $1/2$  mole of  $\text{OH}^-$  per mole of  $\text{Cr}^{3+}$  is measured. By careful dropwise addition of base to a definite quantity of  $\text{Cr}^{3+}$ , the volume of base required to form a permanent turbidity is determined. (The student may need a few tries to find the end point in this highly-colored system, after which his results should be reproducible to the nearest drop of base.) Then  $\text{Cr}^{3+}$  is added until the turbidity dissolves. The turbidimetric determination is repeated for a more dilute solution.

Typical results are given in the table.

| Drops <sup>a</sup> $\text{Cr}^{3+}$<br>(0.51 $M$ ) | Drops <sup>a</sup><br>$\text{OH}^-$<br>(0.55<br>$M$ ) | $pH^b$ | $K_{a1}$             | $K_{dis}$ | $K_{sp}$            |
|--|---|--------|----------------------|-----------|---------------------|
| 20   | 0   | 2.1    | $1.3 \times 10^{-4}$ | ...       | ...                 |
| 20   | 10  | 4.2    | $7.4 \times 10^{-4}$ | ...       | ...                 |
| 20   | 14 <sup>c</sup>                                       | 4.6    | $7.8 \times 10^{-4}$ | 2.3       | $5 \times 10^{-30}$ |
| 20 + 2 <sup>d</sup>                                | 14  | ...    | ...                  | 1.0       | ...                 |
| 11 + 20 $\text{H}_2\text{O}$                       | 9 <sup>d</sup>  | ...    | ...                  | 8.7       | ...                 |

<sup>a</sup> Droppers delivered 17 drops/cc.

<sup>b</sup> Using "pHydrion" short-range papers.

<sup>c</sup> First turbidity.

<sup>d</sup>  $\text{Cr}^{3+}$  added to preceding to dissolve precipitate.

The effects in basic solution are studied by adding base to a small quantity of  $\text{Cr}^{3+}$  and determining the minimum amount required to dissolve the precipitate. (This end point is considerably more difficult than the preceding, as much shaking is required after each addition near the end point to avoid overrunning). Then  $\text{Cr}^{3+}$  is added to  $\text{NaOH}$  solution until a permanent precipitate is obtained.

Typical results are: 5 drops 0.51  $M$   $\text{Cr}^{3+}$  required 27 drops 0.55  $M$   $\text{NaOH}$  to dissolve, or (chromite)/( $\text{OH}^-$ ) = 0.5; 20 drops of  $\text{NaOH}$  required 5 drops of  $\text{Cr}^{3+}$  to form a precipitate, or (chromite)/( $\text{OH}^-$ ) = 5.

Excess  $\text{HNO}_3$  or  $\text{HClO}_4$  is added to a solution of chromite and the color is compared with that of  $\text{Cr}^{3+}$  at comparable concentration.

Observation is made of the changes, including those of color and  $pH$ , that take place when a solution of  $\text{Cr}(\text{NO}_3)_3$ , and also a solution prepared by adding just enough  $\text{NaOH}$  to  $\text{Cr}^{3+}$  to give a precipitate, are heated at 90° for five minutes.

The chromium nitrate solution should be freshly prepared, as sufficient dimer forms on long standing at room temperature (2) to change the  $pH$  significantly. Its concentration and that of the sodium hydroxide should be known to at least 5%. If a student determination is

considered desirable, a direct comparison of the two through a cation-exchange resin may be made. A batch method, using a large excess of resin, is suitable and quite rapid: to 2 g of resin (converted to the H-form and washed several times by decantation) are added 10 drops of  $\text{Cr}(\text{NO}_3)_3$  solution; the system is agitated and let stand for several minutes and then filtered by suction and washed thoroughly. The filtrate is titrated by dropwise addition of the base, using phenolphthalein.

### Discussion

The use of dropwise titration (from a calibrated medicine-dropper)<sup>2</sup> cuts down greatly on the time required, so that a variety of experiments of this sort may be included. The student should recognize, however, that precision is lost and that his experimental results are significant only to an order of magnitude. An important point here is that equilibrium quotients *can* be estimated rapidly and easily.

In organizing the data and comparing with literature values, the student will gain practical experience in the use of the principles of solution stoichiometry and in the algebraic manipulations involving the various forms in which equilibrium data are to be found (acidity or dis-

sociation or formation constants, stepwise or cumulative).

The student should note the irregularity in the order of acid strengths of successive members of the protolytic series derived from  $\text{Cr}^{3+}$ —the fact that  $K_{a3}$  (to solid  $\text{Cr}(\text{OH})_3$ )  $> K_{a1} > K_{a2}$ . This irregularity may be attributed to the existence of the sparingly soluble species,  $\text{Cr}(\text{OH})_3$ . The polymerization phenomena will make the student aware of some of the complexities that exist in the chemistry of the metal ions and of the difficulties in studying them. These phenomena may also be used to introduce ideas in colloid chemistry (an area of study rapidly vanishing from the curriculum).

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<sup>2</sup> Hypodermic syringes, as described by GOODMAN, R. D., and PETRUCCI, R. H., *J. CHEM. EDUC.*, **42**, 104 (1965), would also be appropriate.